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**Fully vulcanized powdery silicone rubber,
preparation and use therof**

The present invention relates to a powdery rubber, more particularly, to a fully vulcanized powdery silicone rubber excluded from vulcanized powdery silicone obtained by chemical crosslinking, a process for preparation and use of the powdery rubber.

It is well known that silicone rubbers can be in the form of blocks, powders, pellets or the like. The vulcanized powdery silicone rubbers have not been disclosed in literatures except the vulcanized powdery silicone rubbers prepared by chemical crosslinking.

A lot of references disclosed the vulcanized powdery silicone rubbers obtained by chemical crosslinking and preparation thereof. For example, U.S.Patent No. 4,743,670 (issued on May 10, 1988) disclosed a highly dispersed vulcanized powdery silicone rubber and preparation thereof. The vulcanized powdery silicone rubber has a uniform particulate shape and particle size, and a bulk resistance of greater than $10^{13} \Omega \cdot \text{cm}$. The process for preparing the vulcanized powdery rubber comprises (1) forming a dispersion of a heat-curable liquid silicone rubber composition in water maintained at a temperature of from 0 to 25°C and in the absence of surfactants, (2) dispersing the resultant dispersion into a liquid maintained at a temperature of at least 50°C to obtain said cured silicone rubber in the form of said finely divided powder, and (3) isolating said powder from said liquid.

U.S.Patent No. 4,742,142 (issued on May 3, 1988) disclosed a process

for preparing a powdery silicone rubber that emulsifying a curable liquid silicone rubber composition in a mixture of water and a surfactant at a temperature of from 0 to 25 degrees C., dispersing the curable composition in water heated to a temperature of at least 25 degrees C. and recovering the resultant cured particles..

U.S.Patent No. 4,749,765 (issued on June 7, 1988) disclosed a process for preparing a powdery silicone rubber having a uniform particle size, which comprises (1) mixing the components at -60 to +5°C to prepare a liquid silicone rubber composition and keep it at the temperature, (2) spraying the liquid silicone rubber composition obtained in step (1) into hot air at 80 to 200°C to effect curing of said composition in the sprayed state, (3) recovering the resultant powdery silicone rubber.

U.S.Patent No. 5,837,793 (issued on November 17, 1998) disclosed a vulcanized powdery silicone rubber obtained from vulcanizable silicone composition and preparation thereof. The powdery silicone rubber has a high hydrophilicity and a soft feel, and an average particle size of less than 500 micron. The process for preparing the powdery silicone rubber comprises (1) vulcanizing a vulcanizable silicone composition comprising a specific polyorganosiloxane to form a vulcanized silicone rubber, and (2) drying the vulcanized silicone rubber by spraying. The vulcanization reaction to form the vulcanized silicone rubber can be addition reaction between the alkenyl groups and the silicon-bonded hydrogen, condensation reaction between the silicon-bonded hydroxyl and silicon-bonded hydrogen, reaction induced by an organic peroxide or UV rays.

Generally, the powdery silicone rubbers disclosed in the above-mentioned reference require using a special silicone rubber

composition as a feedstock, emulsifying it at a lower temperature and using a chemical crosslinking method to obtain the vulcanized powdery silicone rubber. However, the preparation of said special silicone rubber composition as a feedstock and its latex conventionally used in the art are both complex and expensive, and it is difficult to control the particle size and gel content of the powdery silicone rubber obtained by chemical crosslinking, and therefore a fully vulcanized silicone rubber having a sufficiently small particle size cannot be obtained.

Accordingly, it is highly desired in the art of silicone rubber to provide a fully vulcanized powdery silicone rubber having a particle size in nanoscale. In addition, it is also desired in the art to provide a method for preparing a fully vulcanized powdery silicone rubber in a facile manner without the need to use the special silicone rubber composition as the feedstock that is expensive and complex in production, as required in the prior art.

After carrying out intensive and extensive research, the inventor has found that a fully vulcanized powdery silicone rubber can be obtained by subjecting the latex of conventional organosilicon polymer or copolymer having lower molecular weight to irradiation of high-energy rays and then drying. The powdery silicone rubber obtained has a controllable particle size that can reach nanoscale and a controllable gel content. Said rubber powder can be used as toughening agent, processing aids etc., as well as the additives for cosmetics, ink, paints and coatings, and has excellent properties, and thus has a promising prospect and great economical significance.

Therefore, one object of the present invention is to provide a novel fully vulcanized powdery silicone rubber.

Another object of the invention is to provide a process for preparing the fully vulcanized powdery silicone rubber.

Yet another object of the present invention is to provide the use of said fully vulcanized powdery silicone rubber for the above-mentioned objects.

The present invention provides a fully vulcanized powdery silicone rubber in nanoscale. Said fully vulcanized powdery silicone rubber particles have an average particle size of less than or equal to 1μ , usually from 0.02 to 1μ , preferably from 0.05 to 0.5μ , more preferably from 0.05 to 0.1μ .

In the fully vulcanized powdery silicone rubber according to present invention, each particle is homogeneous, without core-shell or multilayer structure inside. In other words, the individual particle is uniform with respect to the composition, and a heterogeneous phenomenon, such as phase-separation structure, within the particles is not detectable with microscopy available nowadays.

The latex of organosilicon polymer or copolymer having lower molecular weight is selected as the feedstock used in present invention, and the particle size of organosilicon polymer or copolymer particles are fixed by irradiation crosslinking. The irradiation-crosslinked latex is then dried to obtain the fully vulcanized powdery silicone rubber. The average particle size of the fully vulcanized powdery silicone rubber particles is dependent on and remains substantially the same as that of particles in the feed latex. The average particle size of the rubber particles in the feed latex of organosilicon polymer or copolymer having lower molecular weight varies with the processing conditions of polymerization. Generally, the particle size can be less than or equal to 1μ , usually from 0.02 μ to 1μ , preferably from 0.05 μ

to $0.5\text{ }\mu$, and more preferably from $0.05\text{ }\mu$ to $0.1\text{ }\mu$. Therefore, the average particle size of the fully vulcanized powdery silicone rubber particles obtained in the present invention may be less than or equal to $1\text{ }\mu$, usually from $0.02\text{ }\mu$ to $1\text{ }\mu$, preferably from $0.05\text{ }\mu$ to $0.5\text{ }\mu$, and more preferably from $0.05\text{ }\mu$ to $0.1\text{ }\mu$.

The latices of organosilicon polymer or copolymer having lower molecular weight used as the feedstock in the present invention include latices of linear or cyclic organosilicon polymer or copolymer having lower molecular weight, preferably linear organosilicon polymer latex having lower molecular weight, such as silicone oil latex, including dimethyl silicone oil latex, diethyl silicone oil latex, methylphenyl silicone oil latex, and methyl hydrosilicone oil latex etc., which are all commercially available. Accordingly, the fully vulcanized powders of such silicone rubbers can be obtained in the present invention.

The present fully vulcanized powdery silicone rubber is a powdery silicone rubber that has a gel content of at least 60% by weight, and is free-flowing without the need of a partitioning agent. If required, the partitioning agent certainly may be introduced into present fully vulcanized powdery silicone rubber so as to further improve the flowability and anti-blocking properties thereof. The present fully vulcanized powdery silicone rubber has a gel content of at least 60% by weight, preferably at least 75% by weight, and more preferably at least 85% by weight. The gel content is a common parameter well known in the art to characterize the crosslinking degree of a rubber, and can be determined by a well-known method in the art.

The present fully vulcanized powdery silicone rubber particle is present in the aggregated form. When the above-mentioned fully vulcanized powdery

silicone rubber is mixed with plastics or other materials, these particles are easy to be uniformly dispersed in the matrix and maintain the particle size of the organosilicon polymer or copolymer particles in the feed latex.

The present fully vulcanized powdery silicone rubber can be obtained by vulcanizing the corresponding rubber latex with irradiation. For example, the specific preparing procedure is as follows: irradiating the organosilicon polymer or copolymer latex having lower molecular weight used as the feedstock, in the presence or absence of a crosslinking agent, through irradiation of high-energy rays, to vulcanize it fully. The irradiation of high-energy rays can be selected from the group consisting of cobalt source, X-rays, UV rays and high-energy electron beams, with cobalt source being preferred. The irradiation dose can be 5 to 30 megarads, preferably 10-20 megarads. The fully vulcanized powdery rubber having a particle size that is substantially the same as the size of the organosilicon polymer or copolymer particles in the latex is obtained by drying the irradiated latex. The drying process can be carried out with spray dryer or by precipitation drying method. If the drying is carried out with a spray dryer, the inlet temperature can be controlled at 100 to 200°C, and the outlet temperature at 20 to 80°C.

In the preparation of the present fully vulcanized powdery silicone rubber, there is no restriction on the kinds of the latex of organosilicon polymer or copolymer having lower molecular weight, wherein the specific examples are as described above, with silicone oil latex being preferred. According to the average particle size of the intended fully vulcanized powdery silicone rubber, the latex of rubber particles having corresponding average particle size is selected as a feedstock. Therefore, the average particle size of rubber particles in the latex can be less than or equal to 1 μ, usually from 0.02 μ to 1 μ, preferably from 0.05 μ to 0.5 μ, and more preferably from

0.05 μ to 0.1 μ . These latices of organosilicon polymer or copolymer having lower molecular weight, such as silicone oil latices, are commercially available.

A crosslinking agent is optionally used in the preparation of the present powdery silicone rubber. The suitable crosslinking agent can be mono-, di-, tri-, tetra- or multi-functional crosslinking agent, and any combination thereof. Examples of said monofunctional crosslinking agent include, but not limited to, isoctyl (meth)acrylate, glycidyl (meth)acrylate; examples of said difunctional crosslinking agent include, but not limited to, 1,4-butandiol di(meth)acrylate, 1,6-hexandiol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, divinyl benzene; examples of said trifunctional crosslinking agent include, but not limited to, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, examples of said tetrafunctional crosslinking agent include, but not limited to, pentaerythritol tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate; examples of said multifunctional crosslinking agent include, but not limited to, di-pentaerythritol penta(meth)acrylate. In the context of the present application, the term "(meth)acrylate" means acrylate and methacrylate.

The above-mentioned crosslinking agent can be used alone or in any combination thereof, as long as it facilitates the vulcanization under irradiation.

The amount of the crosslinking agent added is generally 0.1 to 10% by weight, preferably 0.5 to 7% by weight, more preferably 0.7 to 5% by weight of the solid content in the latex.

The irradiation of high-energy rays used in the present invention is the conventional cobalt source, X-rays, UV rays or high-energy electron beams, preferably cobalt source. In general, the irradiation dose shall be controlled such that after irradiation and vulcanization of the latex, the gel content therein reaches at least 60% by weight, preferably at least 75% by weight, more preferably at least 85% by weight. The irradiation dose can be in the range of from 5 to 30 megarads, preferably from 10 to 20 megarads.

The average particle size of the present fully vulcanized powdery silicone rubber is determined by the transmission electron microscopy.

The gel content of the present fully vulcanized powdery silicone rubber is determined according to the following procedure: placing the irradiated latex on evaporating dish in dropwise manner, and positioning it in a shady and cool place to form a film; after the weight of the film becomes constant, weighing about 0.1 gram of the film, wrapping it with copper screen, and extracting it in toluene until the weight of the thoroughly dried copper screen and film becomes substantially constant, usually for about 8 hours. Then, the thoroughly extracted copper screen and the latex film are dried fully and weighed accurately. The weight ratio of fully extracted film to the original one is defined as gel content.

The present powdery silicone rubber can be used as toughening agent, processing aids etc., as well as the additives for cosmetics, ink, paints and coatings. The basic usage method is to mix the fully vulcanized powdery silicone rubber in the form of dry crosslinked powder or crosslinked latex with matrix materials in a certain ratio, and process with conventional equipment, wherein suitable amount of processing aid and compatibilizers can be added if required. The use of the fully vulcanized powdery silicone rubber

as the modifier for plastics improves physical properties such as the toughness of plastic matrix, and also improves its processing properties and surface gloss.

The present fully vulcanized powdery silicone rubber in the aggregated form has small and uniform particle size, and is very easy to be dispersed in the plastic matrix. It can be mixed with various plastics, as their compatibilizer, processing lubricant or self-lubricant etc., and can be used as additives for cosmetics, ink, paint and coatings, and therefore has great economical significance. In addition, the fully vulcanized powdery silicone rubber is prepared from organosilicon polymer or copolymer latex through irradiation by a simple and inexpensive process, has well controllable particle size and gel content, and is easy to be produced and put into use.

The present invention will be further illustrated in the following by way of the Examples in conjunction with the Figures, which shall not be understood to limit the scope of the invention as defined in the claims.

Figure 1 is a transmission electron micrograph of the silicone rubber particle in silicone oil latex vulcanized by irradiation.

Example 1

5 kg of a commercially available dimethyl silicone oil latex having a solid content of 30% by weight (available from Beijing Second Chemical Factory, Designation: QR-01, with a viscosity-average molecular weight of 146,000) is placed into a container, 75g of trimethylolpropane triacrylate is added dropwise while stirring. The stirring is continued for another 1 hour after the addition is complete. Once mixed uniformly, the latex is irradiated by cobalt source, with the irradiation dose being 20 megarads. The irradiated

latex is spray-dried with a spray dryer, with the inlet temperature being 130 to 150°C, and the outlet temperature being 40 to 60°C. The dried powdery silicone rubber sample 1 is collected in a cyclone separator. The gel content determined is 81%. The particle size of the latex particle vulcanized by irradiation is about 0.2 μ as determined by transmission electron microscopy (see Figure 1).

Example 2

The procedure in Example 1 is repeated except that the irradiation dose used is changed to 15 megarads. A powdery silicone rubber sample 2 is obtained. The gel content determined is 80.5%. The particle size of the latex particle vulcanized by irradiation is about 0.2 μ as determined by transmission electron microscopy.

Example 3

The procedure in Example 1 is repeated except that the irradiation dose used is changed to 10 megarads. A powdery silicone rubber sample 3 is obtained. The gel content determined is 79.1%. The particle size of the latex particle vulcanized by irradiation is about 0.2 μ as determined by transmission electron microscopy.

Example 4

The procedure in Example 1 is repeated except that 30g of divinylbenzene is used as the crosslinking agent. A powdery silicone rubber sample 4 is obtained. The gel content determined is 79.8%. The particle size of the latex particle vulcanized by irradiation is about 0.2 μ as determined by transmission electron microscopy.

Example 5

The procedure in Example 1 is repeated except that 60g of diethylene glycol diacrylate is used as the crosslinking agent and the irradiation dose used is changed to 10 megarads. A powdery silicone rubber sample 5 is obtained. The gel content determined is 80.0%. The particle size of the latex particle vulcanized by irradiation is about 0.2μ as determined by transmission electron microscopy.

Example 6

5 kg of a commercially available dimethyl silicone oil latex having a solid content of 30% by weight (available from Shanghai Resin Factory, Designation: 289 type anionic hydroxysilicone oil latex with a viscosity-average molecular weight of 200,000) is placed into a container, 15g of trimethylolpropane triacrylate is added dropwise while stirring. The stirring is continued for another 1 hour after the addition is complete. Once mixed uniformly, the latex is irradiated by a cobalt source, with the irradiation dose being 15 megarads. The irradiated latex is spray-dried by a spray dryer, with the inlet temperature being 130 to 150 °C, and the outlet temperature being 40 to 60 °C. The dried powdery silicone rubber sample 6 is collected in a cyclone separator. The gel content determined is 80.8%. The particle size of the latex particle vulcanized by irradiation is about 0.15μ as determined by transmission electron microscopy.

Example 7

The procedure in Example 6 is repeated except that the irradiation dose used is changed to 10 megarads. A powdery silicone rubber sample 7 is obtained. The gel content determined is 81.1%. The particle size of the latex particle vulcanized by irradiation is about 0.15μ as determined by transmission electron microscopy.

Example 8

The procedure in Example 6 is repeated except that the irradiation dose used is changed to 5 megarads. A powdery silicone rubber sample 8 is obtained. The gel content determined is 68.8%. The particle size of the latex particle vulcanized by irradiation is about 0.15μ as determined by transmission electron microscopy.

Example 9

The procedure in Example 6 is repeated except that isoctyl acrylate is used as the crosslinking agent. A powdery silicone rubber sample 9 is obtained. The gel content determined is 78%. The particle size of the latex particle vulcanized by irradiation is about 0.15μ as determined by transmission electron microscopy.

Example 10

The procedure in Example 6 is repeated except that the crosslinking agent is absent and the irradiation dose used is changed to 7.5 megarads. A powdery silicone rubber sample 10 is obtained. The gel content determined is 73.5%. The particle size of the latex particle vulcanized by irradiation is about 0.15μ as determined by transmission electron microscopy.